AMPEROMETRIC TITRATION OF METAL IONS WITH EDTA USING AN OXIDE ELECTRODE AS INDICATOR

The Lead (IV) Oxide Electrode, Manganese (IV) Oxide Electrode and Bismith (V) Oxide Electrode

G. Kainz, H. A. Müller and G. Sontag

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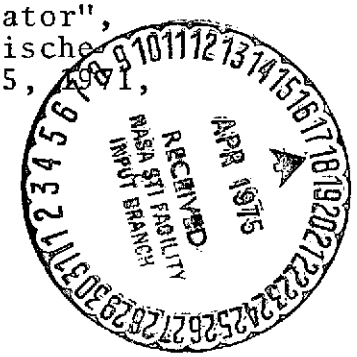

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16. Abstract

An apparatus was developed which indicates the endpoint of chelatometric titrations amperometrically. The most important part of this apparatus is a platinum anode which is coated with a thin film of metal oxide. The cathode is bright platinum. A voltage (between 1.0 and 1.2) is applied to the electrodes. If an excess of EDTA appears after the equivalence, the current between the electrodes rises abruptly. The following metal oxides are suitable: PbO_2, MnO_2, Bi_2O_5 and PtO_x. The conditions for application of these oxide anodes were investigated. The current caused by an excess of EDTA depends on the pH of the solution. The electrodes can be employed between pH 1 and 3, and are suitable for titration of trivalent and tetravalent metal ions. The oxide electrodes described in this paper are valuable complements for the oxide electrodes which we described previously.

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AMPEROMETRIC TITRATION OF METAL IONS WITH EDTA USING AN OXIDE ELECTRODE AS INDICATOR

The Lead(IV) Oxide Electrode, Manganese(IV) Oxide Electrode and Bismuth(V) Oxide Electrode

Gerald Kainz, Hermann A. Müller and Gerhard Sontag

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We have recently found [2] that the electrode pair, Pt (cathode)/Pt-Tl_2O_3 (anode) is outstandingly suitable as an amperometric indicator for EDTA. An optimal signal was obtained for EDTA at pH 5 and 10. This is a pH range which is especially favorable for titration with EDTA. The electrode arrangement, Pt (cathode)/Pt-Co_2O_3 (anode) and Pt (cathode)/Pt-Ni_2O_3 (anode) also proved to be quite useful. The Co_2O_3 electrode yielded a maximal signal for EDTA at pH 3.5 and 10. The Ni_2O_3 electrode, in comparison, was usable only for pH 10.

For the electrodes mentioned, the effective component is the platinum anode covered with an oxide layer. The anode contains only a few micrograms of oxide. The reaction process is as follows: The EDTA which is present in excess after the equivalence point first reduces part of the oxide film, (a)

$$Tl^{3+} + \text{ÄDTA} = Tl^{1+} + \text{ox. ÄDTA} \quad \text{(a)}$$

$$Tl^{1+} = Tl^{3+} + 2e. \quad \text{(b)}$$

The reduced sites of the oxide film are immediately oxidized anodically, with liberation of electrons, (b). The current which flows is recorded and shows the endpoint of the

*Translator's Note: Numbers in margin indicate pagination of original foreign text.

titration, i. e., the excess of EDTA.

Use of the oxide electrodes listed above is limited in the acid range by the fact that because of the acidity of the solution they are dissolved below pH 3, and then no longer respond to EDTA. / 346

Now it is desirable to have electrodes which are resistant to the region between pH 1 and 3, and sensitively indicate EDTA. We found that electrodes coated with the following oxides are suitable for this pH range: PbO_2, MnO_2 and Bi_2O_5. In addition, plain platinum, anodically pretreated, is also usable as an indicator electrode for EDTA. We have investigated the properties of these electrodes in more detail.

I. Lead(IV) Oxide Electrode

Preparation. Two platinum electrodes were immersed in a 0.001 M lead(II) nitrate solution, which was adjusted to pH 9.4 after addition of Rochelle salt. Now there are two possibilities for forming: a) at constant current (e. g., 15 μA); duration of forming, 5-10 minutes; b) at constant voltage (e. g., 1.2 V). At constant voltage, the electrolysis begins at a current of about 70 μA; but the current decreases rapidly and approaches a constant value after about 20 minutes (see Figure 1). The oxide deposited is more fine-grained the lower the current is in forming. Also, the oxide film is more homogeneous at pH 9.5 than at pH 4.5. Therefore, we recommend deposition at a constant 15 μA.

1. Composition of the oxide layer

The composition of the oxide layer formed at pH 9.5 was determined. In order to have a large amount available, we extended the duration for formation to 200 minutes and performed

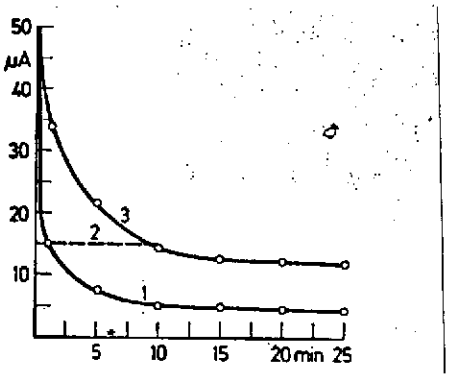

Figure 1. Formation of the PbO_2 electrode, current curve. a) at constant voltage (E 1.2 V): 1 at pH 4.5; 3 at pH 9.5. b) at constant current: 2, 15 μA.

the experiment at different electrolysis voltages (0.6 to 1.4 V). It appeared that: the oxide layer contains not only Pb^{4+} (determined iodometrically) but also a constant amount of Pb^{2+}. As only Pb^{4+} is deposited anodically, then Pb^{2+} must be formed secondarily, through reduction. The cause of this is the Rochelle salt, which was added as a complex former at pH 9.5. This reduces part of the electrolytically formed PbO_2 to PbO. The latter, however, remains embedded in the lattice of the oxide film.

2. Indication of EDTA

The conditions under which the PbO_2 electrode responds to EDTA were tested.

a) Effect of the applied polarization voltage.
We applied various polarization voltages to the electrode pair, Pt (cathode)/Pt-PbO_2 (anode). We determined: a) the current

flowing between the electrodes in the presence of a buffer (pH 4.5); b) the current flowing after the addition of 0.20 ml EDTA (0.01 M). Figure 2 shows that a maximal signal is obtained at a polarization voltage of 1.2 V (6 μA for 0.20 ml EDTA). There is practically no indication of EDTA at a polarization voltage of more than 1.6 V.

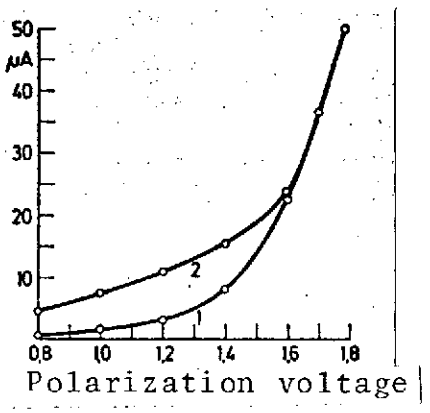

Figure 2. Determination of the optimal polarization voltage. 1. Buffer (pH 4.5). 2. Buffer + 0.2 ml EDTA (0.01 M).

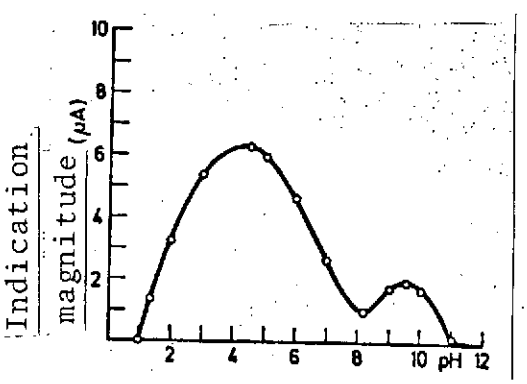

Figure 3. Signal from the PbO_2 electrode for 0.2 ml EDTA at different pH values.

b) Effect of the pH value.

We obtained a signal for EDTA between pH 1 and pH 11; but the signal height differs (see Figure 3). The first maximum is at /347
pH 4.5 (6.3 μA/0.2 ml EDTA). The second maximum is at pH 9.5 (2 μA/0.2 ml EDTA). Between, there is a minimum at pH 8 (1 μA/0.2 ml EDTA). For analytical purposes, the signal height should be at least 1 μA/0.10 ml EDTA. Thus, one can use the PbO_2 electrode between pH 1.5 and 7.5. Use at pH 10 is possible, of course, but there are considerably more sensitive electrodes available, such as the Tl_2O_3, Co_2O_3, and the Ni_2O_3 electrodes.

II. Manganese(IV) Oxide Electrode

Preparation. Two platinum electrodes are immersed in a 0.001 M manganese(II) sulfate solution, buffered to pH 4.5, and 5 μA is applied for 10 minutes. Some 5 μg of dark-brown MnO_2 deposits on the anode.

a) Optimal polarization voltage. This was determined at pH 2.5. It is 1.0 V. No indication of EDTA with MnO_2 can be detected above 1.5 V.

b) Dependence of the signal height on the solution pH. With MnO_2 also we found a differing signal height, depending on the pH. The electrode responds to EDTA between pH 1.5 and pH 7. There is a maximum at pH 2.5 (11.5 μA/0.2 ml EDTA). For analytical purposes, the signal between pH 1.7 and just barely pH 4 is high enough to be usable for the titration (see Figure 4).

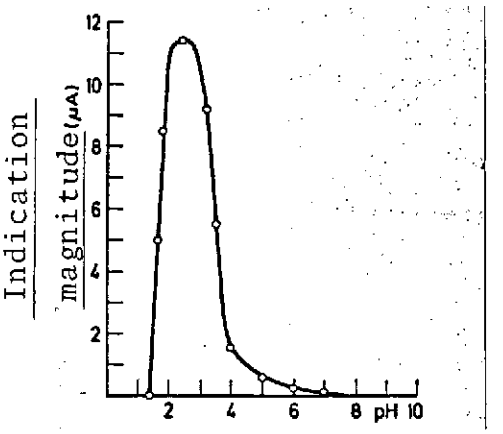

Figure 4. Signal from the MnO_2 electrode for 0.2 ml EDTA at various pH values.

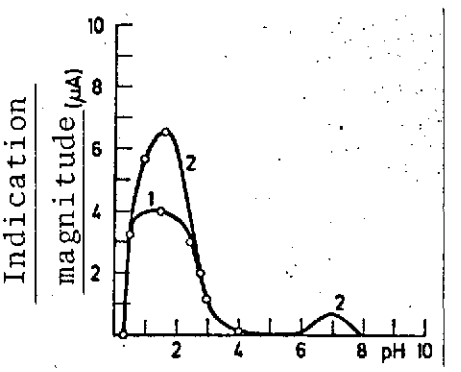

Figure 5. Signal from the Bi_2O_5 and PtO_x electrodes for 0.2 ml EDTA at different pH values. 1. Bi_2O_5 electrode. 2. PtO_x electrode.

III. Bismuth(V) Oxide Electrode

Preparation. The electrolyte is a 0.001 M bismuth nitrate solution, adjusted to pH 11.5 to 12 with KOH after addition of tartrate. At a voltage of 1.5 V, black Bi_2O_5 separates after a few minutes. No oxide formation occurs at pH 10 (buffer: NH_3/NH_4^+) or at voltages less than 1.4 V.

a) Optimal polarization voltage. This was determined at pH 1.5, and is 1.4 V. The electrode dissolves slowly at a potential below 1.3 V. EDTA is no longer indicated above 1.6 V.

b) Dependence of the signal on pH. As Figure 5, No. 1, shows, the Bi_2O_5 electrode gives a signal for EDTA between pH 0.5 and 4.0. The maximum indication is at pH 1.5 (4 µA/0.2 ml EDTA). The indication is analytically useful between pH 0.7 and pH 2.7.

IV. Platinum Oxide Electrode

Preparation. Two platinum electrodes are immersed in a solution of nitric acid (pH about 2.5), and a potential of 1.2 V is applied. The current flowing decreases in the course of 20 minutes from 65 µA to 7 µA, and is then practically constant (see Figure 6). After this the electrode is usable for the titration.

a) Optimal polarization voltage. This was determined at pH 1.7, and is 1.2 V.

b) Signal height and pH of the solution. An indication is obtained for EDTA between pH 0.5 and pH 3.5, and between

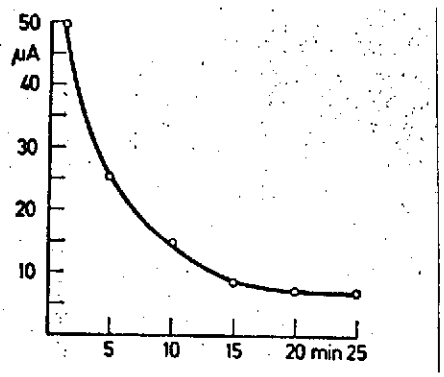

Figure 6. Forming of the platinum oxide electrode, current curve.

pH 6 and pH 8. The first maximum is at pH 1.7 (6 µA/0.2 ml EDTA), the second maximum is at pH 7 (0.7 µA/0.2 ml EDTA). The electrode is usable between pH 1 and pH 3 (see Figure 5, No. 2).

c) Signal height and duration of forming. The electrode / 348 was formed for various times at pH 1.7 with constant voltage (1.2 V). Then we added 0.2 ml EDTA and determined the signal height. This first rises linearly with the duration of forming, attains a maximum value after 8-10 minutes, and then remains approximately constant.

d) Composition of the oxide film. While the (anodic) oxide deposition was visually detectable with the other electrodes, this is not the case with platinum. But the following points indicate the formation of a platinum oxide (on the surface): a) the contact resistance of the platinum anode rises sharply in the forming. b) the signal height (for EDTA) rises with the duration of forming. c) the platinum anode gives a blue color with iodide-starch. The amount of iodine liberated, however, is only a few micrograms.

V. Course of the Reaction

As we have already mentioned [2], a redox reaction occurs between the oxide (on the anode) and EDTA. EDTA reduces part of the oxide. But then the reduced sites are immediately oxidized anodically. Visually, one can detect no change in the oxide layer. The electrons liberated from the anode are indicated by the measuring equipment.

At excessively high polarization voltage (1.6 V and above) there is no change in current on addition of EDTA. In this case, EDTA is oxidized directly at the anode, through the oxygen developed. Then the oxide does not participate in the reaction.

The extent of the reaction between the oxide and EDTA rises with the acidity of the solution; likewise, the signal changes. But there are limits to the increase, because any oxide will go into solution below a certain pH value. Then the EDTA signal falls to zero.

Now, how large is the amount of EDTA converted at the oxide electrode? To determine this it was necessary to know the oxygen consumption in the reaction EDTA/oxide. We mixed 0.8 g PbO_2 with 0.2 ml 0.01 M EDTA solution at pH 4.5 and heated the mixture briefly with boiling water. 4.85 ml of CO_2 and 1.0 ml of O_2 formed. The amount of CO_2 formed indicates that EDTA is oxidized completely to CO_2 (and H_2O).

Huber and Tallant [1] were previously concerned with the oxygen development. According to them, EDTA promotes the decomposition of PbO_2 (to Pb^{2+} and O_2), with Pb^{2+} being removed continuously from the equilibrium.

For complete oxidation, EDTA requires 20 equivalents of oxygen, or 40 Faradays. Thus, we can calculate the amount of EDTA effectively converted at the oxide electrode. In the range of the maximum, 6 μA flows. If one follows the indication for 100 seconds, for instance, then 0.045 μg EDTA is oxidized in this time.

This shows that the chemical conversion at the oxide electrode is extremely small and practically negligible. But the current change of 6 μA caused by this reaction can be recorded quite well.

VI. Analytical Application of the Oxide Electrodes.

a) At pH 1-2. The electrodes with MnO_2, PtO_x and Bi_2O_5 are suitable. But the MnO_2 electrode is preferable because of its higher sensitivity. Titratable ions are: Fe^{3+}, Bi^{3+}, Tl^{3+}, Th^{4+}, Zr^{4+}.

b) At pH 4.5. The PbO_2 electrode is suitable here. Admittedly, the MnO_2 electrode can be used at this pH, but it is less sensitive. Titratable: Hg^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ce^{3+}, La^{3+}, Sc^{3+}. The Tl_2O_3 and Co_2O_3 electrodes can also be used in this region.

Experimental Portion

Forming solutions. Lead(II) nitrate: 0.001 M; manganese(II) sulfate: 0.001 M; Bismuth(III) nitrate, 0.001 M.

Equipment. Polarograph (Metrohm E 261) for generation of the polarization voltage and for measurement of the current flowing between the electrodes. Polarizer (Metrohm E 456) for forming the electrodes. Double platinum electrode (Metrohm EA 210).

Preparation of the oxide electrodes. The double platinum electrode is immersed in the solutions specified above. The appropriate pH value is adjusted (see above), and the electrode is formed at constant current. Forming is done at constant voltage only for the platinum oxide electrode.

Titration. The formed electrode pair is placed in the sample solution. The solution is buffered and the optimal polarization voltage is applied. One waits until the current has become constant (about 5 minutes). The sensitivity of the polarograph is set to 10^{-6} to 10^{-8} A/mm. Then 0.01 M EDTA solution is added, and the current curve is recorded. Evaluation is done graphically by extrapolating the curve branches.

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